

LIQUEFACTION OF A SUBBITUMINOUS COAL IN THE PRESENCE OF NOVEL MICROEMULSION-BASED MOLYBDENUM CATALYSTS

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INTRODUCTION

The state of knowledge in catalysis of direct coal liquefaction has been reviewed recently by Derbyshire (1988). An efficient catalyst for coal solubilization and/or upgrading of coal liquids not only improves the yield and distribution of products but relaxes some of the stringent demands placed upon the (process-derived) solvent. An inexpensive, disposable catalyst, which does not have to be recycled or recovered, is of particular interest for improved process economics (and thus commercialization potential). Use of "dispersed" catalysts (i.e., catalysts which are "unsupported" or initially supported by the coal prior to its dissolution) has been of increasing interest in recent years (Utz et al., 1989; Cugini et al., 1991; Hirschon and Wilson, 1991; Miki et al., 1991; Bi et al., 1991), particularly for the dissolution stage of coal liquefaction, but also for liquid upgrading purposes. In most studies, the relatively expensive molybdenum-based catalysts have been found to provide greater rate enhancement (at comparable catalyst loadings) than the inexpensive iron-based catalysts. (Both are probably most active in their (at least partially) sulfided form.) Derbyshire (1988) correctly concludes, however, that "there is usually insufficient information available on catalyst dispersion and composition to provide a sound basis for direct comparison" and that "the available information on catalyst dispersion is totally inadequate."

The objective of our work is to use a novel approach to synthesize direct liquefaction catalysts of known particle size (and thus known dispersion). It is based on the molecular design of metal-loaded reverse micelles (microemulsions). In particular, the synthesis and catalytic testing of nanosize molybdenum sulfide particles is of interest. In this regard, the approach taken here differs from the early work at the Dow Chemical Company (Moll and Quaderer, 1979) in which micrometer-size particles were obtained by emulsifying a solution of AHM in a recycle oil. The emphasis in this paper, which reports the results of our initial efforts, is on the synthesis and use of molybdenum-based catalyst particles but the techniques being developed should also be generally applicable.

EXPERIMENTAL SECTION

Microemulsion Catalyst Synthesis. Molybdenum sulfide particles were synthesized in three different microemulsion systems: (a) 0.1 M sodium bis (2-ethylhexyl) sulfosuccinate (AOT)/decane/water (b) 0.1 M polyoxyethylene nonylphenyl ether (NP-5)/cyclohexane/water, and (c) 0.4 M NP-5/tetralin/benzyl alcohol/water. The use of an anionic (AOT) and a nonionic (NP-5) surfactant was thus explored. The microemulsions were prepared at room temperature by first adding 10% sulfuric acid to the oil/surfactant solution. The acid-solubilized microemulsion was deoxygenated by bubbling nitrogen through it for 20 min. This procedure was followed by adding 10^{-3} , 10^{-3} and 10^{-2} M ammonium tetrathiomolybdate (ATTM) to the AOT/decane, NP-5/cyclohexane and NP-5/tetralin/benzyl alcohol systems, respectively. Additional information on the microemulsion synthesis procedures are given in a companion publication (Boakye et al., 1992). To investigate the effect of particle size on liquefaction kinetics, the water-to-surfactant molar ratio was varied during microemulsion formulation.

For comparative purposes, molybdenum catalysts were also prepared in a conventional manner, by excess-solution impregnation. The catalyst precursor was ammonium heptamolybdate (AHM). It was dissolved in deionized water, at 1 % (wt) Mo loading. Five grams of coal were added to this solution and stirred overnight at 60 °C. The impregnated coal was dried under vacuum for 48 h at room temperature. In selected experiments, the pH of the solution was adjusted to 2.5 using formic acid.

Coal Liquefaction. Conventional liquefaction experiments were conducted following the procedures used previously at Penn State (Derbyshire et al., 1986; Davis et al., 1991). The coal (2.5 g), tetralin (5 g) and carbon disulfide (0.12 g) were charged into a standard (25 cc) tubing bomb reactor and agitated for 30 min in a preheated fluidized sand bath. The reaction conditions were: 350 ± 2 °C, 1000 psig H_2 (cold). In the case of microemulsion-based NP-5/cyclohexane catalysts, the microemulsion was added to 2.5 g of coal; no tetralin was used. Tetralin was added to the AOT/decane system. The NP-5/tetralin/benzyl alcohol catalyst system was also simply added to 2.5 g of coal in the tubing bomb reactor. "Blank" microemulsions, without the molybdenum catalyst, were also tested.

After reaction, the tubing bomb was rinsed with hexane into a weighed ceramic thimble. The reaction products were extracted with hexane in a conventional Soxhlet extractor assembly for 12-18 h, until the solvent falling back into the flask was absolutely colorless. The hexane was removed in a rotary vacuum evaporator and the product left behind (referred to as oils) was weighed. The thimble with the residue (referred to as residue) was dried and weighed. The reaction yields are thus reported as weight percent oils (hexane solubles) plus gases; gas production at the relatively low temperature of 350 °C was not very significant, however.

RESULTS AND DISCUSSION

A Wyodak subbituminous coal was used in this study. Its properties are summarized in Table 1. Figure 1 shows the plot of the average particle size vs. the water-to-surfactant molar ratio (R) for molybdenum sulfide in the 0.4 NP-5/tetralin/benzyl alcohol microemulsion. It is interesting to note that an optimum R value exists for which a minimum particle size of ca. 40 nm was obtained.

Tables 2 and 3 show the yield of oils (plus gas) in liquefaction tests using the AOT/decane and NP-5/cyclohexane microemulsions. At comparable Mo loadings, the yields are lower for the latter system, possibly due to the absence of a hydrogen donor solvent, whose role is crucial for low-rank coals when an efficient catalyst is not available to meet the relatively high hydrogen demand (Derbyshire and Stansberry, 1987).

Table 4 illustrates the use of NP-5/tetralin microemulsions for R values of 1-4. The oil (plus gas) yield is seen to be remarkably high at low Mo loadings. Furthermore, a comparison with the data in Figure 1, as well as those in Table 3, suggests that there is an optimum water-to-surfactant ratio for which the average particle size is at a minimum and the yield of oils at a maximum. (The oils produced are relatively viscous, suggesting that they contain some higher-molecular-weight (hexane-soluble) components.)

Table 5 was compiled in an attempt to place our initial results into proper perspective. For a subbituminous coal, high oil yields were obtained by Weller and Pelipetz (1951), when the catalyst precursor was added to the coal in an acidic medium. This could be due either to the favorable interaction with the coal or to a more effective sulfidation of the catalyst. It should be noted, however, that our attempt to maximize the dispersion of the catalyst at pH=2.5 by favoring the electrostatic interaction between the positively charged coal surface and molybdate anions (Solar et al., 1990) was not successful.

Hirschon and Wilson (1991) have recently reported relatively high yields (~84%) of toluene-solubles (corresponding roughly to the sum of asphaltenes, oils and gases) for an Illinois No. 6 bituminous coal (425 °C, 500 psi H₂, 20 min) using an organometallic Mo complex, with 0.6 mmol Mo/g coal, i.e., 5.8% Mo. The use of an organometallic Fe complex resulted in yields of ~40% (in the absence of a hydrogen donor solvent), with ~3.4% Fe. Also using "dispersed-phase" Mo catalysts (1000 ppm of ATTM, MoS₃, AHM), Utz et al. (1989) obtained yields of ≤60% heptane-solubles for a bituminous coal (425 °C, 1000 psi H₂, 1 h). Similar results were reported more recently for "dispersed-phase" Fe catalysts by Cugini et al. (1991).

Under appropriately selected conditions, the microemulsion-based catalysts are seen to be able to produce comparable yields of oils at much lower Mo loadings.

CONCLUSIONS

Our initial results on the kinetics of coal liquefaction in the presence of microemulsion-mediated molybdenum sulfide particles are very encouraging. Yields of oils which are equal or superior to those obtained using conventional catalyst preparation techniques are achieved at molybdenum loadings that are lower by one order of magnitude. At a more fundamental level, the variation in the water-to-surfactant molar ratio, during the formulation of the microemulsion system, offers the possibility to vary catalyst particle size and surface area over a wide range. This in turn allows the testing of correlations between liquefaction kinetics and catalyst dispersion.

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Table 1
Characteristics of Low-Rank Coal Used in the Liquefaction Experiments

Penn State Sample Bank Number	PSOC 1401
Seam	Lower Wyodak
State	Wyoming
ASTM Rank	Subbituminous B
Mean Maximum Vitrinite Reflectance, %	0.42
Ultimate Analysis, % daf	
Carbon	72.23
Hydrogen	4.59
Nitrogen	1.06
Sulfur (total)	0.29
Oxygen (by difference)	21.83
Proximate Analysis	
Moisture	16.33
Volatile Matter	37.74
Fixed Carbon	41.14
Ash	4.79
Petrographic Composition (% vol, mf)	
Vitrinite	85.0
Liptinite	2.0
Inertinite	13.0

Table 2
Preliminary Results of Liquefaction Tests with the
AOT/Decane Microemulsion Catalyst

Run #	Sample	Mo Loading	Yield of Oils (+Gas), %	% Residue
4	Coal/Mo ME	1.2 ppm	33.8	66.2
8	Coal/Mo ME	2.6 ppm	47.9	52.1

Table 3
Results of Liquefaction Tests with the 0.1 M NP-5/Cyclohexane
Microemulsion (ME) Molybdenum Sulfide Catalyst

Run #	Sample	Mo Loading	Yield of Oils (+Gas), %	% Residue ^a
17	Coal/Mo ME (R=0.5)	1.9 ppm	14.1	85.9
18	Coal/Mo ME (R=1)	2.0 ppm	19.9	80.1
19	Coal/Mo ME (R=2)	2.0 ppm	20.5	79.5
20	Coal/Mo ME (R=3)	1.9 ppm	14.4	85.6
21	Coal/ME ^b	0.0 ppm	4.6	95.4

^a Includes preasphaltenes and asphaltenes

^b Surfactant plus cyclohexane alone

Table 4
Results of Liquefaction Tests Using 0.4 M NP-5/Tetralin/Benzyl Alcohol
Microemulsion (ME) Molybdenum Sulfide Catalyst ^a

Run #	Sample	Mo Loading	Yield of Oils (+Gas), %	% Residue ^b
23	Coal/Mo ME (R=1)	58 ppm	78.4	21.6
24	Coal/Mo ME (R=2)	118 ppm	83.2	16.8
26	Coal/Mo ME (R=3)	185 ppm	9.1	90.9
27	Coal/Mo ME (R=4)	243 ppm	9.9	90.1
29	Coal/ME (R=1)	0.0 ppm	7.3	92.7
30	Coal/ME (R=2)	0.0 ppm	5.2	94.8
31	Coal/ME (R=3)	0.0 ppm	2.9	97.1
32	Coal/ME (R=4)	0.0 ppm	6.2	93.8

^a Coal/tetralin = 1/2.5-2.6

^b Includes preasphaltenes and asphaltenes

Table 5
Compilation of Results of Liquefaction Tests on Subbituminous Coals
Using Conventional Catalysts

Author(s)	Coal	Conditions	Catalyst	Yield of Oils (+Gas), %
Weller and Pelipetz (1951)	Subbit. B	450 °C, 1 h 1000 psi H ₂	None	10.4
Weller and Pelipetz (1951)	Subbit. B	450 °C, 1 h 1000 psi H ₂	AHM ^a (1% Mo)	41.1
Weller and Pelipetz (1951)	Subbit. B	450 °C, 1 h 1000 psi H ₂	AHM ^b (1% Mo)	76.5
Epstein (1987) (see Burgess et al., 1991)	Subbit. B	425 °C, 10 min 1000 psi H ₂	None	37.8
Epstein (1987) (see Burgess et al., 1991)	Subbit. B	425 °C, 10 min 1000 psi H ₂	SAM ^c (1% Mo)	24.9
Epstein (1987) (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	None	32.0
Epstein (1987) (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	SAM (1% Mo)	44.0
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	350 °C, 1 h 1000 psi H ₂	None	11.2
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	350 °C, 1 h 1000 psi H ₂	SAM (1% Mo)	14.0
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	350 °C, 1 h 1000 psi H ₂	STM (1% Mo)	14.7
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	None	16.9
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	SAM (1% Mo)	21.7
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	STM (1% Mo)	30.7
This study	Subbit. B	350 °C, 30 min 1000 psi H ₂	AHM/CS ₂ (1% Mo)	70.2
This study	Subbit. B	350 °C, 30 min 1000 psi H ₂	AHM/CS ₂ (1% Mo) ^g	71.1
This study	Subbit. B	350 °C, 30 min 1000 psi H ₂	None	29.1

^a AHM = ammonium heptamolybdate

^b AHM acidified with H₂SO₄

^c SAM = sulfided ammonium molybdate

^d 350 °C, 1 h; 425 °C, 10 min

^e STM = sulfided tetrahydroquinolinium molybdate

^f ATTM = ammonium tetrathiomolybdate

^g pH adjusted to 2.5 during catalyst impregnation

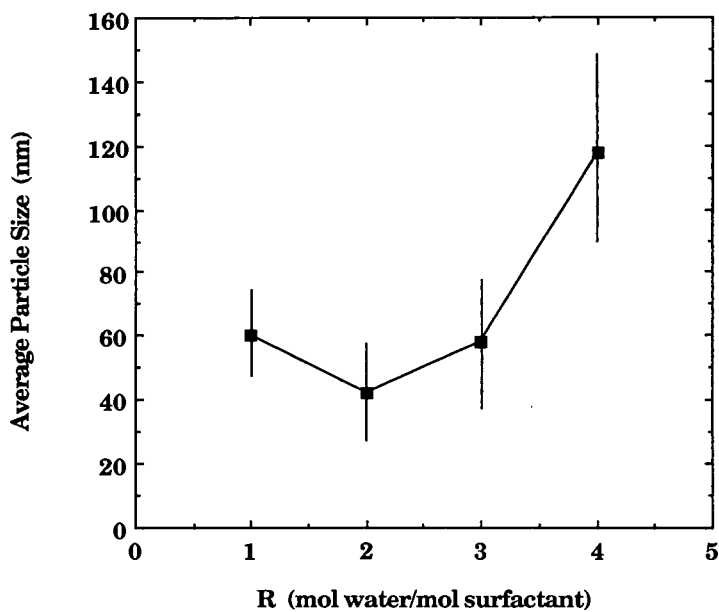


Figure 1. Effect of water-to-surfactant molar ratio (R) on the average particle diameter for the 0.4 M NP-5/tetralin/benzyl alcohol microemulsion.